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EVALUATION OF REGENERATIVE FUEL CELL

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1. SUMMARY

The objective of this program has been the evaluation of the effects of the important and controllable parameters on the performance characteristics of a regenerative hydrogen-oxygen fuel cell. Eventual consideration was to have been given to the construction of a flight-weight prototype for a specific application.

At the start of this program in March 1961 a leak proof, corrosion resistant model had been developed and shown to operate effectively for many cycles with no apparent degradation in the temperature range of 180 to 320°F (denoted as cell A). All of the important parameters which had been shown to affect the voltage and current efficiency of this model had been established.

The first program objective for the past six months was to obtain quantitative relationships between the important parameters and the voltage and current efficiency. When this was accomplished the investigations were to be directed towards the determination of the factors affecting charge retention and capacity.

The first objective was successfully completed during the first three months, and the second objective during the last three months.

The second half of the program proved to be the most beneficial to the realization of a flight-weight model. Until that time the charge retention and capacity were known to be very limited. But as a result of the analyses and investigations carried on during the last three months the modifications necessary for greatly increasing the level of these characteristics were established. (The modified cell is denoted as cell B). The improvements resulted in a charge retention increase by a factor of 38 and a capacity increase from 7 amp-minutes to 3 amp-hours. Further improvements are expected from continued development.

Another significant accomplishment during the contract period was the obtaining of experimental evidence to establish that the electrochemical reactions within the cell are limited to those of the hydrogen and oxygen half cells. A final result was the recognition of the predominant type of polarization.

Recommendations are suggested for continued development in two areas. The first area consists of the continued study of the factors affecting charge retention. If this characteristic can be improved to an even greater extent than has already been achieved, then the applications for the cell will be more general. The second area consists of the evaluation of new oxygen electrodes. If a better oxygen electrode is found then the voltage and power efficiency could be raised to a higher level than is currently attainable.

2. STATUS AT START OF PRESENT PROGRAM

At the start of this program in March 1961 a leak proof, corrosion resistant cell (denoted as cell A in this report) had been developed and shown to operate effectively for many cycles without any apparent degradation. The effects of the most important variables on voltage and current efficiency had been established and shown to include the operating temperature, electrolyte content, and electrode preparation.

The most critical variable was shown to be the preparation of the hydrogen electrode. By giving this porous nickel electrode a lithiating treatment similar to the one given the oxygen electrode the cell performance had been shown to be markedly improved.

This latter result was not established until the latter part of the preceding program. Hence one of the recommendations for the initial phase of the current program was to repeat a parameter study with this new hydrogen electrode. In this manner the conditions could be specified for maximum current and voltage efficiency.

The completion of the above study would not, however, complete the evaluation of this cell. As of the beginning of this program very little information had been obtained on the important characteristic of charge retention and capacity. Quantitative data was required. Other important areas for investigation were the measurement of internal cell pressures and the verification that the electrochemical reactions within the cell are limited to those of the hydrogen-oxygen reactions.

The facilities for carrying out the present program were adequate and the experimental techniques were well developed. The facilities included three constant-current cycling units, three single track recorders, three ovens and several cell frames. The electrode fabrication technique had been perfected to the point where several identical

electrodes could be prepared, starting with the raw nickel powder, within two days. The assembly of leak-tight cells by the use of a double "O" ring was also well established.

3. REVIEW OF PROGRAM OBJECTIVES

The principal objective of the current program has been the quantitative evaluation of the effects on fuel cell performance produced by the important and controllable parameters. The fuel cell performance was to be measured in terms of the following:

- a. Current efficiency
- b. Voltage efficiency
- c. Capacity
- d. Stand time

The controllable parameters include:

- a. Electrode material
- b. Electrode treatment
- c. Electrolyte content
- d. Internal geometry
- e. Operating temperature

The experimental results should comprise engineering data needed for preliminary designs of the fuel cell for specific applications. Eventual consideration was to be given to an operating cycle consisting of 65 minutes charge, 35 minutes discharge.

An additional objective was to establish that the electrochemical reactions within the cell are limited to those of the hydrogen-oxygen reactions. A final objective was to measure the pressure variations within the cell.

4. SUMMARY OF EXPERIMENTAL PROGRAM

The important and controllable parameters for cell A (cf. Sec. 6) were temperature, electrolyte content, electrode preparation, and void space (the internal cell volume containing no asbestos). The voltage and current efficiencies of this model were determined for the 65/35 cycle for the following ranges of the parameters:

Temperature: 220 to 340°F

Electrolyte Content: 0.65 to 1.07 cc of 35 percent
KOH solution per gram of asbestos

Void Space: 0 to 75 percent

Electrode Preparation: held constant (see Sec. 5.1)

The polarization data for this model was determined over a wide range of current densities from 0 to 300 ma/cm², and at temperatures between 220°F and 320°F.

Additional investigations included the measurement of internal cell pressure and the determination of charge retention and capacity.

The important and controllable parameters of cell B (cf. Sec. 6) are temperature, electrolyte content, pressures, electrode preparation, and bed thickness. Due to the limited time that was available for the evaluation of this model the parameters have not been varied to any great extent. The bed thickness has been fixed at 1/16 inch and the electrolyte content at 0.5 cc of 35 percent KOH per gram of asbestos. The electrode preparation has been varied, but the evaluation was carried out on a separate primary cell model. The charge retention and capacity of cell B have been determined at both room temperature and 200°F. The polarization data was obtained over a range of current densities from 0 to 75 ma/cm² at both room temperature and 200°F.

5. EXPERIMENTAL TECHNIQUES

5.1 Electrodes for Cell A

The electrodes for cell A were prepared by pouring nickel powder (Metals Disintegrating grade 151) into an alumina mold and sintering in a hydrogen atmosphere for one hour at 1350°C. The lithiating treatment consisted of soaking the electrode in a lithium hydroxide solution followed by oxidizing in air at 700°C for 5 minutes. The concentration of the lithium hydroxide solution was 11.15 gm/100 ml of distilled water for the heavily lithiated oxygen electrode and 2.23 g/100 ml for a lightly lithiated hydrogen electrode.

5.2 Electrodes for Cell B

Identical platinized nickel electrodes were employed for both hydrogen and oxygen electrodes in cell B. These electrodes were prepared by immersion plating of a porous nickel sheet in a 3 percent solution of chloroplatinic acid. The porous nickel plates were obtained from Gould National Batteries, designated as "raw unimpregnated plates." The amount of solution employed was fixed on the basis of depositing 40 mg of platinum per square inch of nickel sheet.

5.3 Pressure Measurement in Cell A

A pressure transducer with range of 0 to 500 psi was installed in cell A. The transducer was recessed 1/16 inch into the wall behind one electrode. A perforated plate was used to cover the transducer so as to avoid making a zero adjustment to compensate for the pressure of the asbestos against the transducer. The unit was calibrated before and after each test. An additional check on the calibration was made by comparison of the indicated pressure reading before charge with the vapor pressure of water at the given cell temperature.

5.4 Cycling Performance of Cell A

During the initial phase of this program the characteristics of cell A were all determined on the basis of a fixed cycle which consisted of a 65 minute charge and a 35 minute discharge. The charging current was arbitrarily fixed at a constant value of 25.8 ma/cm^2 for all runs. The discharge current was set so that the state of complete discharge, as signified by a rapid drop in voltage, occurred at the end of the 35 minute discharge.

5.5 Leak Testing

Cell A was leak tested by immersion in a water bath in the fully charged state. Due to the double "O" ring seal a leak was very seldom found.

Cell B was leak tested by several methods. When first assembled it was pressurized with nitrogen at 100 psi and the various fittings were given the "soap bubble" test. After having located the leaks and tightened the connections the cell was again pressurized with nitrogen at 100 psi and let stand overnight. On the first few trials the pressure was always found to drop several pounds, but the leaks could not be located. Subsequently when all the thread fittings were wrapped with Dupont "Tape Dope" the pressure was found to hold overnight at 100 psi. The cell was then assumed to be leak proof.

5.6 Temperature Measurements

The cell temperatures were measured with an iron-constantan thermocouple inserted in a small hole in the cell body. The readings were taken with a Rubicon potentiometer.

5.7 Polarization Measurements

The polarization data for both cells was obtained by use of the constant current units. The procedure consisted of setting the current to a given value for either charge or discharge and then measuring the resultant cell voltage on the recorder. After each change in the current setting a time interval of approximately 3 minutes was required before

the cell voltage reached a steady state value. Several current settings were made to correspond to current densities between 0 and 300 ma/cm².

The internal cell resistance was measured by use of an impedance bridge operating at 1000 cycles.

5.8 Charge Retention

The charge retention tests consisted of three steps. First the cell was charged at a constant current for a given time interval. Then the cell was allowed to stand on open circuit for a given time interval. Finally the cell was discharged at constant current until the voltage had dropped to zero. The loss of charge expressed as a percentage of the initial amp-hour input was divided by the stand time in hours to give the loss per unit of time.

5.9 Capacity

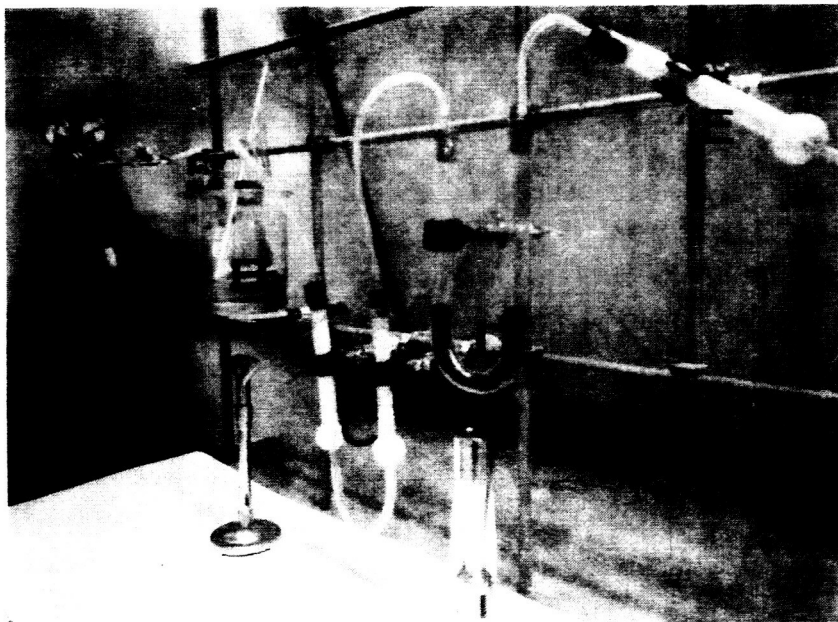
The capacity of cell A was determined by a special technique. First the cell was charged for one minute at a constant current of 200 ma. Immediately after the end of charge the cell was discharged completely. The time of discharge was recorded. Next, the cell was charged for 5 minutes at 200 ma. Again, the cell was discharged at the same current and the time of discharge recorded. This procedure was repeated for runs of 10, 20, 40, and 80 minutes.

The input and corresponding output in terms of amp-minutes were then calculated and the results plotted. The resultant curve indicated that a maximum output existed. This value was taken as the capacity.

The ultimate capacity of cell B has not yet been determined. A discussion of the capacity of this cell is given in Sec. 7.15.

5.10 Hydrogen Storage Capacity of Negative Electrode

The hydrogen content of the negative electrode of cell A was determined by use of the apparatus shown in Fig. 1. The major components consisted of a heated tube filled with copper oxide and a calcium chloride drying tube. The function of the copper oxide was to convert the hydrogen to water while the function of the calcium chloride was to collect the water.



- A. Nitrogen cylinder
- B. Sample flask
- C. Calcium chloride tubes
- D. Copper oxide tube
- E. Calcium chloride tube

FIG. 1 APPARATUS FOR DETERMINATION OF HYDROGEN
IN ELECTRODES

In operation the charged electrode was placed in the heated flask into which nitrogen was continuously passed. The hydrogen which was evolved from the electrode was swept into the copper oxide tube and the water formed in this tube was swept into the weighed calcium chloride tube. The amount of hydrogen was calculated on the basis of the amount of water collected. The two calcium chloride drying tubes between the sample flask and the copper oxide tube were used to collect any water which had been absorbed by the electrode or the nitrogen.

5.11 Oxygen Electrode Evaluation

The evaluation of several oxygen electrodes was carried out by inserting them in a primary hydrogen-oxygen fuel cell and measuring the voltage-current curve of the cell on discharge. A common hydrogen electrode, platinized nickel, was used in all runs. Two layers of 1/32 inch asbestos saturated with 35 percent KOH were used as the electrolyte. Since no special precautions were taken to minimize the internal resistance of this primary cell, the current densities which it delivered were relatively small. However the differences in cell voltage at a given current density, brought about by the use of the various oxygen electrodes, were large enough to be significant.

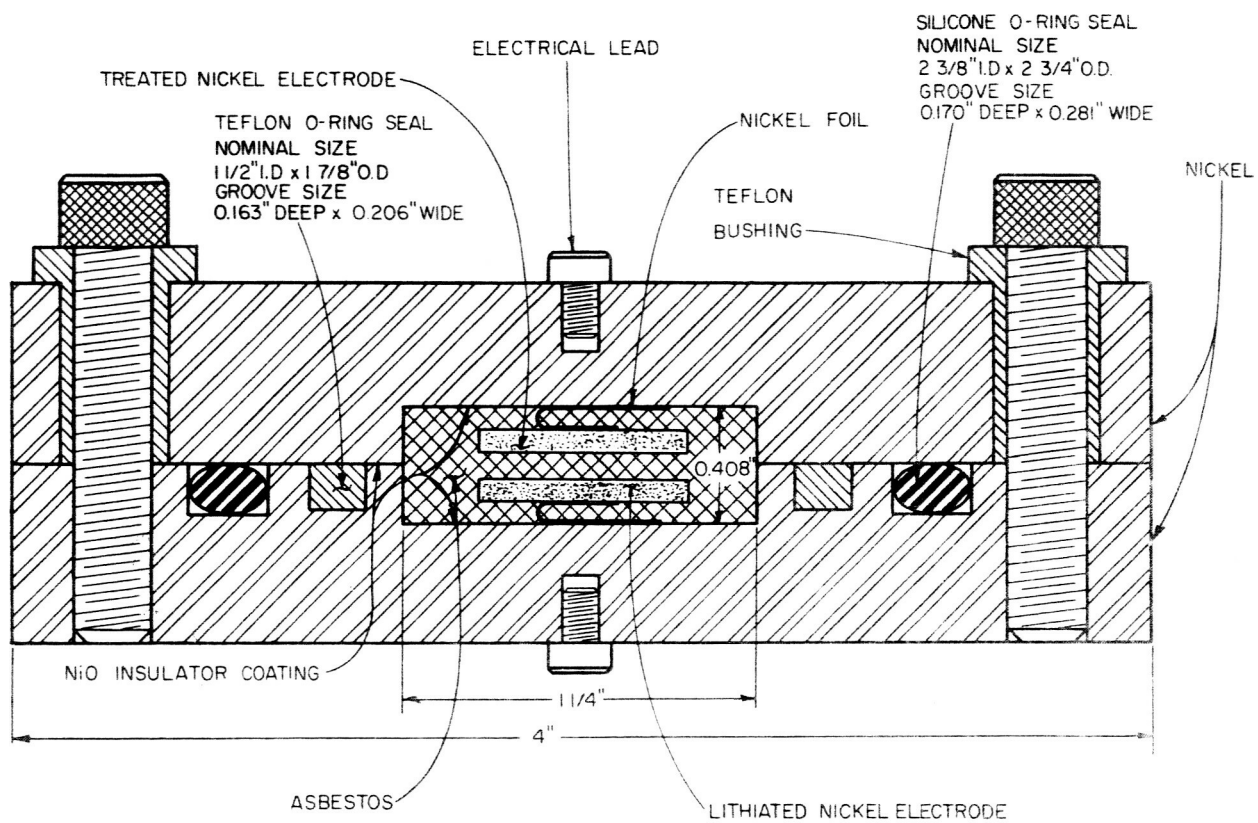


FIG. 2 COMPONENTS OF CELL A

6. DESCRIPTION OF EXPERIMENTAL CELLS

A description of the experimental cells which have been employed in the present program is given in the following sections.

6.1 Description of Cell A

The components of cell A are shown in Fig. 2 and are described below:

- a. Hydrogen electrode: sintered porous nickel disc, 15/16 inch diameter, 1/8 inch thick, lightly coated with lithiated nickel oxide.
- b. Oxygen electrode: identical to hydrogen electrode except more heavily lithiated.
- c. Cell frames: pure nickel, machined to contain electrodes plus asbestos, surface oxidized to form non-conductive nickel oxide.
- d. Internal configuration: electrodes parallel and separated by layer of 1/32 inch thick asbestos; space between electrodes and frames filled in with asbestos; thin nickel strips connected to each electrode and its respective cell frame.

This cell has an operating temperature range of approximately 200°F to 320°F. Therefore, it must be placed in an oven for testing. No adjustments are necessary, i.e., it is merely heated to temperature and operated as any secondary battery.

6.2 Description of Cell B

The components of cell B are shown in Fig. 3 and the cell assembly, within an oven, in Fig. 4. A description of the components is given below:

- a. Hydrogen container: 2 inch diameter stainless steel pipe with welded caps, 240 cc volume.

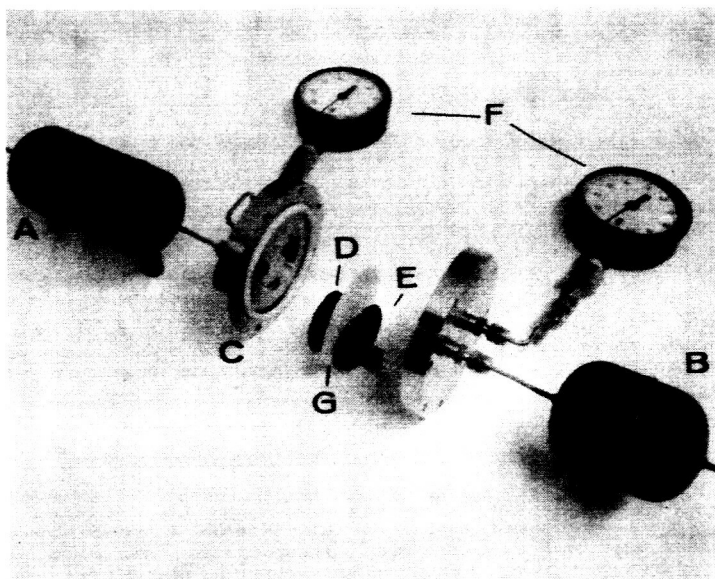


FIG. 3
COMPONENTS OF CELL B

- A. Hydrogen container
- B. Oxygen container
- C. Cell frame with "O" ring
- D. Hydrogen electrode
- E. Oxygen electrode
- F. Pressure gages
- G. Asbestos bed

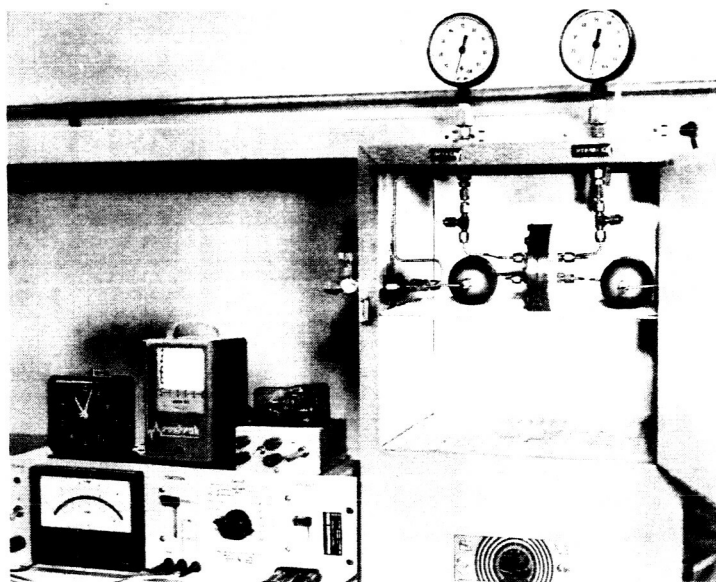


FIG. 4
ASSEMBLY OF CELL B

- b. Oxygen container: same material as hydrogen container, 120 cc volume.
- c. Cell frames: 4 inch diameter stainless steel, recessed for electrodes and "O" ring groove.
- d. Hydrogen electrode: 1-5/8 inch diameter, .022 inch thick disc of wire reinforced sintered nickel, coated with platinum black at 20 mg per square inch.
- e. Oxygen electrode: same as hydrogen electrode.
- f. Electrolyte: 35 percent KOH solution impregnated in disc of asbestos 2-1/2 inch diameter by 1/16 inch thick.

The compression of the asbestos around its outer edge by the two steel frames seals the two gas compartments from one another. The "O" ring eliminates external leaks. Insulated metal bolts around the perimeter of the frames hold the two halves tightly together.

After the cell is assembled, the two gas cylinders are flushed with their respective gases. This step is a necessity for if it were not taken the hydrogen formed on charge would react chemically with the residual air (O_2) on the platinized electrode and create a temporary vacuum.

After the two gas compartments are flushed, the cell can be operated in the same manner as any secondary battery.

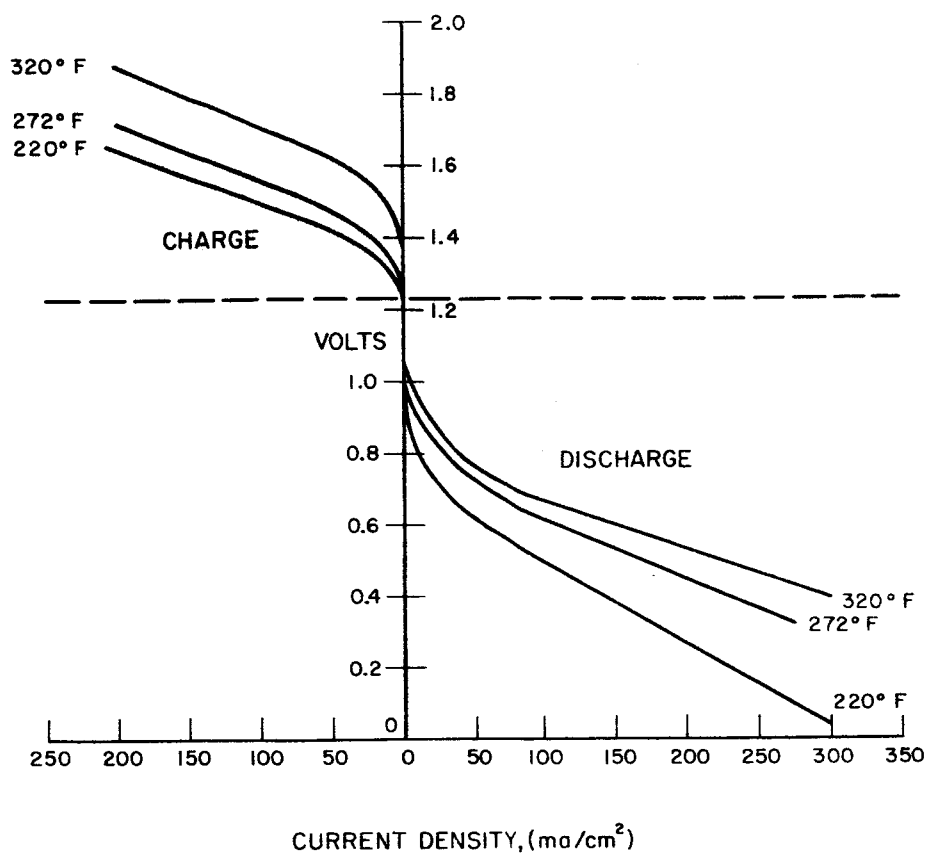


FIG. 5 VOLTAGE-CURRENT CURVES OF CELL A

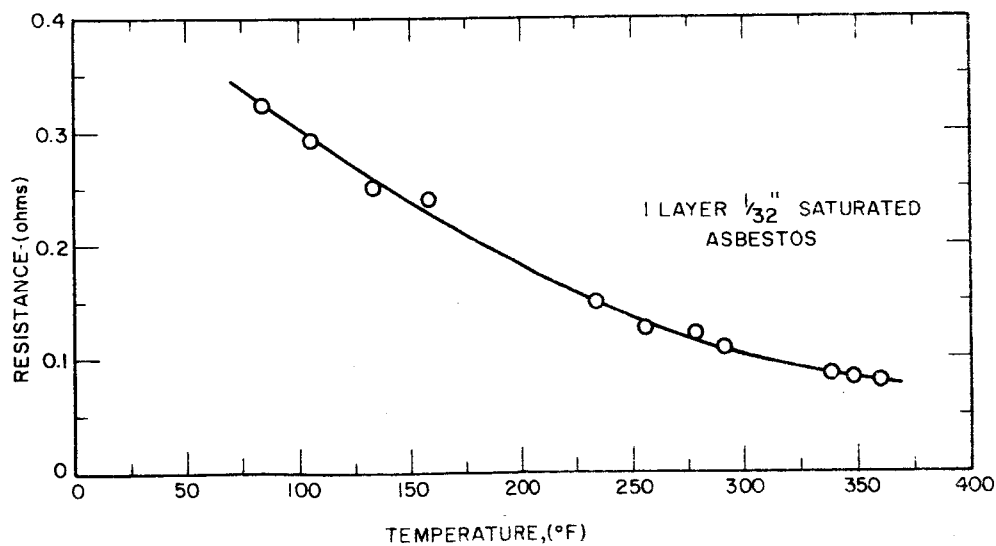


FIG. 6 INTERNAL RESISTANCE VS. TEMPERATURE OF CELL A

7. EXPERIMENTAL RESULTS AND DISCUSSION

The performance characteristics of cells A and B are described in the following sections. The characteristics of cell A are presented in Sec. 7.1 to 7.11 and those of cell B in Sec. 7.12 to 7.17.

7.1 Voltage-Current Characteristics of Cell A

The relationship between the voltage of cell A and its current density is shown in Fig. 5. The horizontal line at 1.23 volts gives the theoretical open circuit voltage for the hydrogen-oxygen reaction. At a given current density for either charge or discharge the difference between the cell voltage and 1.23 volts gives the total cell polarization. Inspection of Fig. 5 reveals that the total cell polarization is markedly reduced by an increase in temperature. This phenomena is in accord with the theory of polarization (Ref. 2). Another point worth noting is that the polarization at a given current density is somewhat larger for discharge than for charge.

7.2 Temperature Versus Internal Resistance of Cell A

The internal resistance of cell A was measured at several temperatures from 82°F to 360°F. A plot of the cell resistance versus temperature is given in Fig. 6. As noted, the cell resistance decreases with an increase in temperature. This phenomena can be explained by the fact that the resistance of the electrolyte solution as well as that of the semiconductor electrodes decreases with an increase of temperature (Ref. 3 and 4).

7.3 Components of Cell A Polarization

The total cell polarization consists of the three component parts, i.e. ohmic, concentration, and activation (Ref. 5). Knowing the internal cell resistance the ohmic polarization can be calculated as the product of the current density and internal cell resistance. This

value can then be subtracted from the total polarization to give the activation-concentration component.

These calculations were carried out and the results plotted in Figs. 7 and 8. Inspection of these figures reveals that the activation-concentration component constitutes the major portion of the total cell polarization. The ohmic portion is smaller but not negligible. The shape of the activation-concentration polarization curve indicates that the concentration component is negligible (Ref. 6). Hence the activation polarization constitutes the major portion of the total polarization.

7.4 Bed Thickness Versus Internal Resistance of Cell A

The contribution of the asbestos bed to the internal cell resistance was determined by varying its thickness and observing the change in cell resistance. The resistance of cell A, containing respectively 1, 2, and 4 layers of 35 percent KOH impregnated asbestos (1/32 inch per layer) between the two electrodes, was measured at 280°F. The values of the internal resistance were plotted and are presented in Fig. 9.

The dotted "theoretical" curve which passes through the origin corresponds to a case where the asbestos bed constitutes 100 percent of the total resistance. The experimental curve however, does not pass through the origin but intercepts the resistance axis (zero bed thickness) at a finite value of 0.09 ohms. This result signifies that the asbestos bed constitutes only a part of the total cell resistance. The balance must be due to the resistance of the semiconductor electrodes as well as the resistance of various internal contacts.

7.5 Effect of Temperature and Electrolyte Content on Cycling Performance of Cell A

The effects of operating temperature and electrolyte content on the performance of cell A are shown in Table I.

The results indicate a number of trends. First, the voltage efficiency tends to increase with an increase in operating temperature. This trend is in accord with the reported performance of other cells as

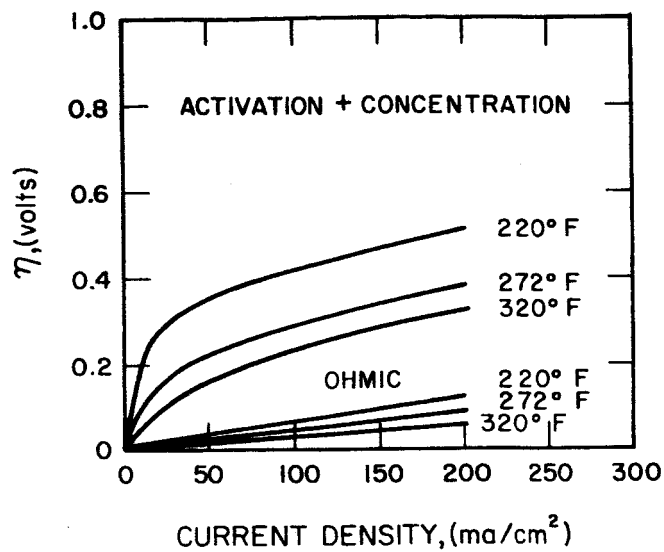
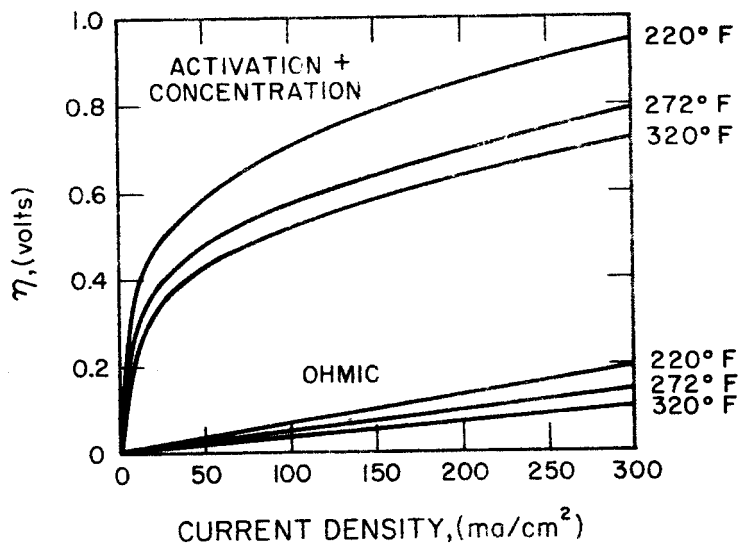


FIG. 7
COMPONENTS OF CHARGE
POLARIZATION FOR CELL A

FIG. 8
COMPONENTS OF DISCHARGE
POLARIZATION FOR CELL A



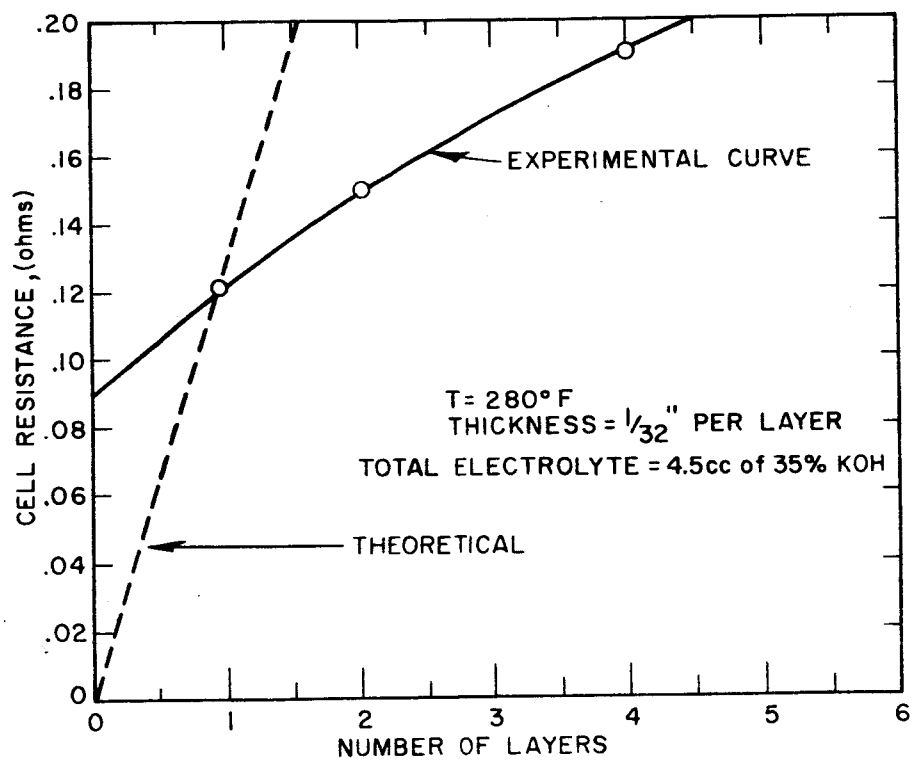


FIG. 9 BED THICKNESS VS. INTERNAL CELL RESISTANCE OF CELL A

TABLE I EFFECT OF TEMPERATURE AND ELECTROLYTE CONTENT ON CYCLING PERFORMANCE OF CELL A

ELECTROLYTE CONTENT cc of 35% KOH per gm of asbestos	TEMPERATURE (°F)	VOLTAGE		VOLTAGE EFFICIENCY (Percent)	CURRENT DENSITY		CURRENT EFFICIENCY (Percent)
		Charge Volts	Discharge Volts		Charge (ma/cm ²)	Discharge (ma/cm ²)	
0.65	220	1.76	0.1	10	25.8	2	< 5
0.65	272	1.64	0.1	10	25.8	2	< 5
0.84	222	1.61	0.76	47	25.8	12.9	27
0.84	228	1.61	0.76	47	25.8	18.0	38
0.84	278	1.51	0.85	57	25.8	23.2	49
0.84	333	1.41	0.94	67	25.8	16.8	35
0.90	280	1.43	0.80	55	25.8	34.8	65
0.97	220	1.64	0.82	50	25.8	25.3	53
0.97	280	1.52	0.96	63	25.8	23.2	49
0.97	280	1.48	1.20	81	5.7	5.7	54
1.07	228	1.59	0.81	51	25.8	20.3	43
1.07	280	1.50	0.86	57	25.8	20.3	43
1.07	340	1.42	0.96	68	25.8	7.7	16*

*Gas Leak

well as the data in Sec. 7.2. For best voltage efficiency, therefore, the cell should be operated at as high a temperature as is feasible.

Second, the cell performance as measured by current efficiency optimizes at a particular temperature. At an electrolyte content of 0.90 cc of 35 percent KOH per gram of asbestos, the optimum current efficiency corresponds to a temperature of about 278°F. At temperatures much lower than 228°F and higher than 333°F the current efficiency drops to very low values. In order to obtain good current efficiencies (> 40 percent) the cell should be operated at temperatures well within this range and preferably close to 278°F.

Third, again based on current efficiency, an optimum electrolyte content exists. Near 280°F a maximum current efficiency of 65 percent is obtained with an electrolyte content of 0.90 cc of 35 percent KOH per gram of asbestos. At electrolyte contents only slightly higher than 1.07 or slightly lower than 0.65 cc of KOH per gram of asbestos (say 10 percent), the current efficiency drops to very low values. A second condition for obtaining high current efficiency, then, is to employ an electrolyte content greater than 0.65 cc and preferably close to 0.90 cc of 35 percent KOH per gram of asbestos.

7.6 Effect of Void Space on Current Efficiency of Cell A

Farlier data has indicated that if the internal volume of cell A adjacent to and behind each electrode was not completely filled in with asbestos, then the cell performance was low. As a consequence, quantitative data on the effect of this parameter was determined by measuring the current efficiency with the internal volume completely filled with asbestos (void space = 0 percent), and with a large portion of the asbestos removed (void space = 75 percent). The electrolyte content, 0.90 cc of KOH per gram of asbestos, and temperature 280°F were held constant for both conditions. The following results were obtained:

<u>VOID SPACE</u> <u>(PERCENT)</u>	<u>CURRENT EFFICIENCY</u> <u>(PERCENT)</u>
0	63
75	38

These results indicate that the addition of void space adversely affects performance, and as a consequence, in order to obtain the best current efficiency, the internal cell volume adjacent to the electrodes should be completely filled in with asbestos.

The effect of void space is peculiar to this particular cell model and the cause has not yet been established.

7.7 Hydrogen Storage in Cell A

The theory of operation of cell A was based on the assumption of hydrogen storage in the negative nickel electrode. According to the procedure described in Sec. 5.10 the amount of hydrogen contained within this electrode was determined. The results of several determinations are given below.

<u>Sample</u>	<u>Mg Water Collected</u>	<u>Equivalent Amp-minutes of Hydrogen</u>
Charged Electrode No. 1	14	-
Uncharged Electrode No. 1	3	-
Net Water Collected	11	1.95
Charged Electrode No. 2	13	-
Uncharged Electrode No. 2	3	-
Net Water Collected	10	1.77

These results tend to verify that the negative nickel electrode does contain hydrogen. Although the amount of hydrogen, expressed in terms of the equivalent ampere-minutes, is below the experimentally determined maximum capacity of 7.0 ampere-minutes, the loss can be accounted for. Either some hydrogen was lost during the transfer of the electrode from the cell to the flask or the analysis time may have been insufficient for all of the hydrogen to be liberated. Nevertheless, the data does indicate that hydrogen is present.

7.8 All Liquid No Asbestos Experiment in Cell A

In order to examine the question of the nature of the cell reactions in cell A (Ref. 7), an "all liquid-no asbestos experiment" was formulated. Specifically, the objective was to establish that the cell reactions are limited to those of the H_2-O_2 half-cells.

It is known that the gas electrodes of the H_2-O_2 cell can deliver but a very small current density when completely flooded (Ref. 8). Therefore, if the electrodes of cell A were completely flooded and its current efficiency found to be very low, the implication would be that the two half-cell reactions, or at least one of them, must be that of the H_2-O_2 cell.

This experiment was carried out by removing all of the asbestos and completely filling the internal cell volume with 35 percent KOH. The current efficiency was measured and found to have a very low value of 10.3 percent.

This result gives additional support to the interpretation that the cell reactions are limited to those of the hydrogen-oxygen half-cells.

7.9 Pressure Variations in Cell A

In order to gather further information related to the nature of the cell reactions, an attempt was made to measure the pressure variations within cell A. The intended test procedure was to record the pressure variations for several 100 minute cycles at the same current densities as shown in Table I. The first test was conducted at a charging current of 100 ma (25.8 ma/cm^2). After several minutes of charge, the pressure was observed to be increasing at such a rate that the range of the transducer would be exceeded long before the end of the 65 minute charging period. Consequently, the test procedure was discontinued.

Subsequently, the cell was charged at 50 ma (12.9 ma/cm^2). At the end of 40 minutes, the allowable range of the transducer was reached, and as a consequence, the cell was discharged. After 15 minutes of discharge at 50 ma, the pressure had dropped to 330 psi and the voltage had dropped to zero. Finally, with a residual pressure of 330 psi the cell

was charged at a current of 20 ma (5.1 ma/cm^2). At the end of 15 minutes the allowable range of the transducer was again reached. The cell was again discharged, and again when the cell pressure reached 330 psi, the voltage fell to zero (see Fig. 10).

Additional pressure data for longer charge times are needed in order to interpret the foregoing results. One important observation can be cited, however, as a result of the fact that the cell voltage drops to zero while the cell is still under high pressure. This occurrence implies that some of the absorbed hydrogen is desorbed, mixed with the oxygen, and subsequently becomes unavailable for electrochemical reaction.

7.10 Capacity of Cell A

The capacity of cell A was determined by the procedure described in Sec. 5.3. For the conditions specified in Fig. 11 the results indicate that a maximum output of approximately 7 amp-minutes is all that can be obtained from cell A, no matter how large the input. This value is taken as the cell capacity.

7.11 Charge Retention of Cell A

An examination of the measured performance characteristics of cell A indicated the need for obtaining quantitative data on its charge retention or "stand time" characteristics. This determination was carried out in the manner described in Sec. 5.8.

The result, shown in Fig. 12, is expressed in terms of the percent of the output that was attainable immediately after the end of the charge versus the time after the end of charge. The slope of this curve, which gives the approximate loss per unit of time, was found to be 0.75 percent per minute. Thus, the cell loses all of its charge in slightly over two hours.

At the present time, this result signifies that the applications of cell A with no further improvements in charge retention are limited to a condition of continuous cycling for relatively short cycle times, i.e., 100 minutes.

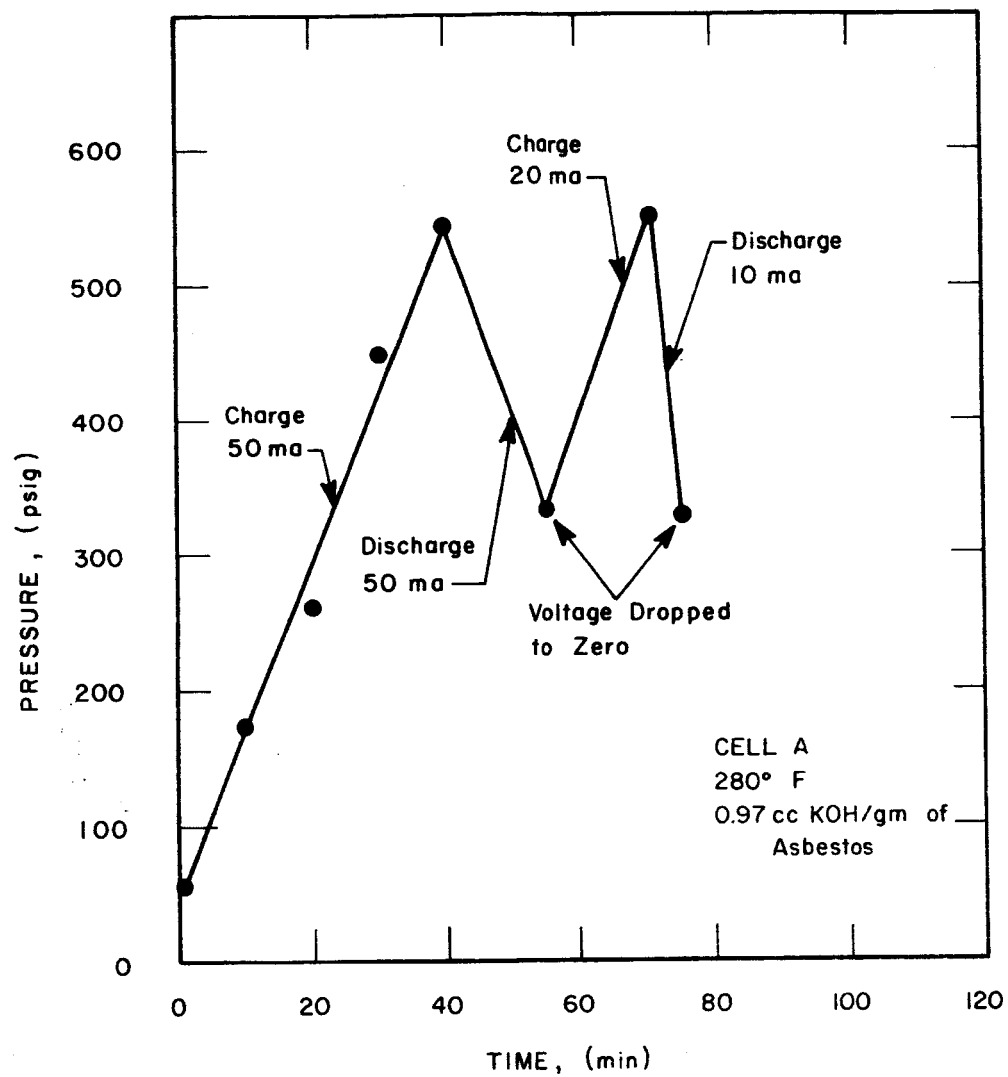


FIG. 10 PRESSURE VARIATION IN CELL A

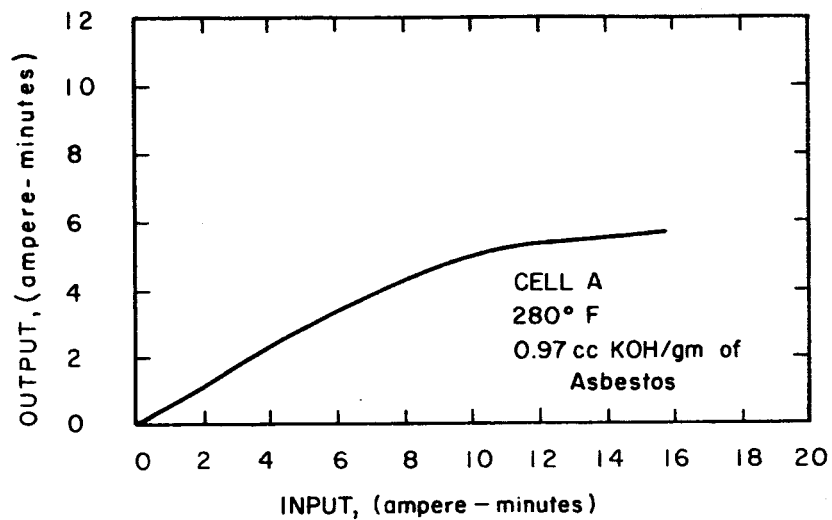


FIG. 11 CAPACITY OF CELL A

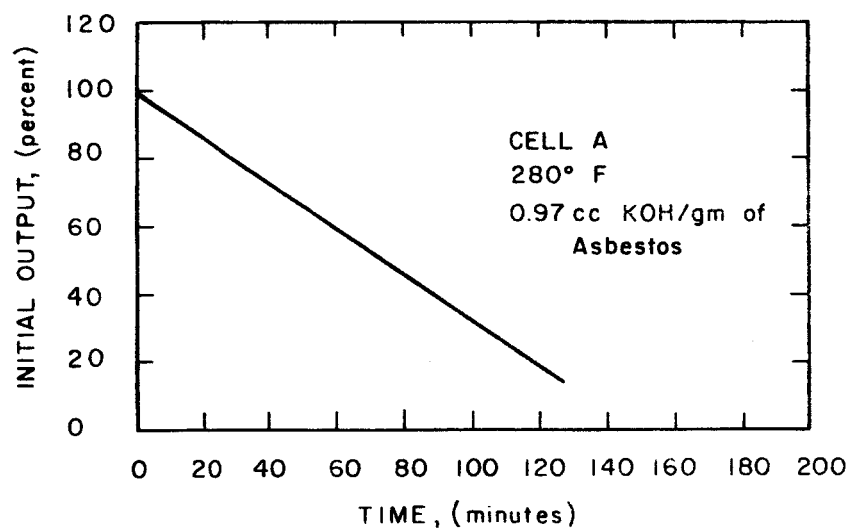


FIG. 12 CHARGE RETENTION OF CELL A

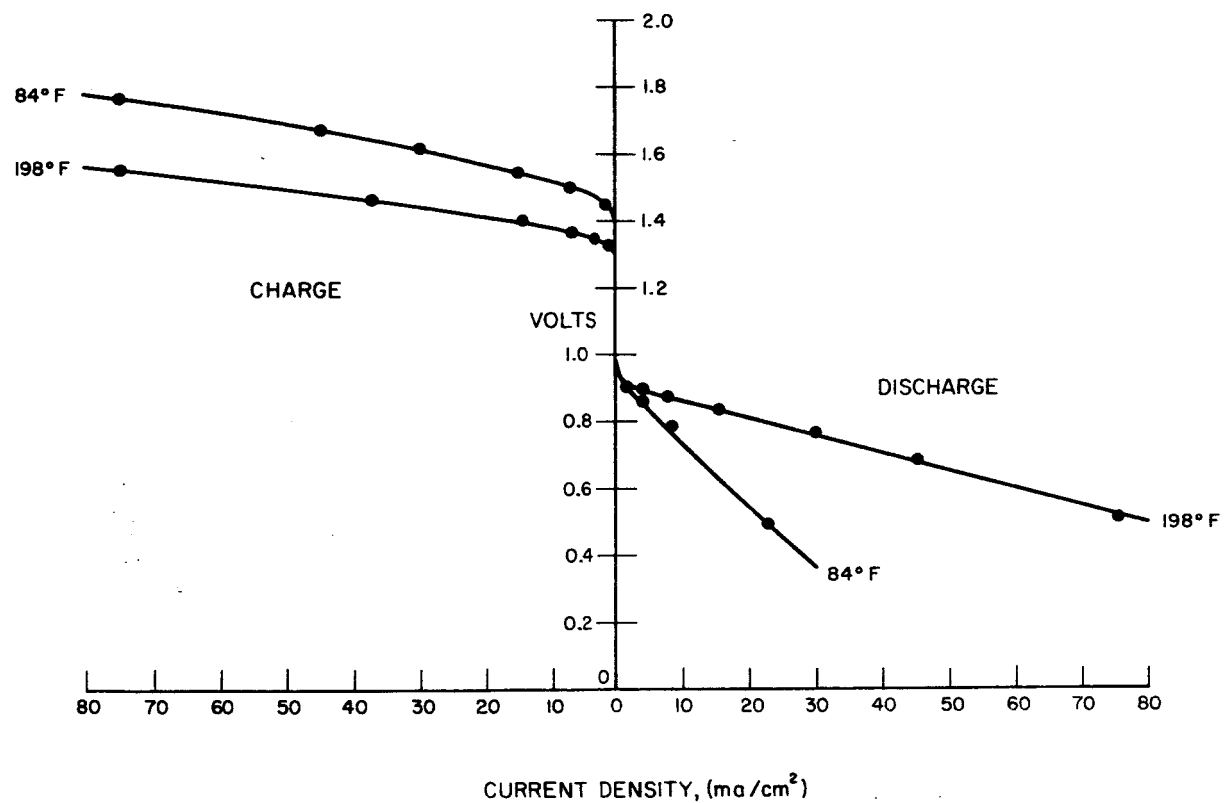


FIG. 13 VOLTAGE-CURRENT CURVES OF CELL B

The loss of charge in this cell is undoubtedly due to the chemical reaction between the oxygen and the hydrogen. The rapidity of this thermal recombination is readily explainable on the basis of the large differential pressure between the two gases, i.e., the oxygen which is stored at pressures greater than 500 psi can rapidly diffuse through the pores of the asbestos to the surface of the negative electrode and there react with the absorbed hydrogen.

In order to eliminate this large pressure differential and reduce the gaseous diffusion rate through the bed, the design of cell B was developed. The feasibility of this new design in overcoming the rapid charge loss is described in Sec. 7.13.

7.12 Voltage-Current Characteristics

The voltage-current characteristics of cell B were determined at both room temperature and at 198°F (see Fig. 13).

Inspection of Fig. 12 reveals that the total cell polarization for both charge and discharge is appreciably decreased as the operating temperature is raised. For example, at 25 ma/cm² on discharge the voltage is 0.48 volts at 84°F and 0.77 volts at 198°F.

A comparison of the voltage-current curves for cells A and B reveals a very close similarity. However, the slopes of the curves for cell B are somewhat greater than for cell A indicating a higher internal resistance. The higher resistance of cell B can be explained in part by the larger distance separating its electrodes, 1/16 inch for cell B versus 1/32 inch for cell A. Another contributing factor is the lower operating temperatures which were employed for the first series of tests. The linearity and high slope at 84°F indicate a high ohmic polarization near room temperature.

As with cell A, the shape of the voltage-current curves again reveals that appreciable activation polarization is present. This type of polarization is again more prevalent on discharge than on charge. Most likely this polarization is due to the oxygen electrode. Attempts to reduce this polarization have been and are currently being made by evaluating new oxygen electrodes. This study is presented in Sec. 7.17.

7.13 Charge Retention of Cell B

The charge retention characteristics of Cell B were found to be much greater than those of cell A. However, the need still exists for improving the charge retention to an even greater extent before this cell is ready for general application.

The first test was conducted on the low pressure lucite cell model with ehrlenmeyer flasks as gas containers. This cell was found to retain 90 percent of its charge after a one hour stand time at 200°F. Thus, this cell lost its charge at a rate of 0.16 percent/min, i.e., a five fold decrease over that of cell A. This result signified that the particular design of cell B was much better suited than cell A for retaining charge.

Next the high pressure stainless steel cells were evaluated. Only two such tests have been conducted to date with these models. One cell which was charged to 60 psig retained 64 percent of its charge after a 19-1/2 hour stand time at 200°F. The second cell, which was also charged to 60 psig, retained 78 percent of its charge after a 16-1/2 hour stand time at 80°F. These results correspond respectively to an increase by factors of 25 and 38 in charge retention over that of cell A.

Additional charge retention tests have been outlined for a wide range of conditions. Operating temperatures will range from room temperature to 300°F and pressures from atmospheric to 500 psig. The tests will be conducted for stand times up to 72 hours. Since one of the important factors is believed to be the thickness of the asbestos bed, its effect will also be examined.

7.14 Discharge Characteristics of Cell B

The cell voltage is continuously recorded during each run by a miniature Rustrack recorder. The voltage-time data was taken from the chart for two such runs and is presented in Figs. 14 and 15.

In Fig. 14 is shown the discharge voltage versus time at 84°F. As indicated the cell voltage remained relatively constant near 0.7 volts as a current of 200 ma (15.1 ma/cm^2) was withdrawn from the cell for a

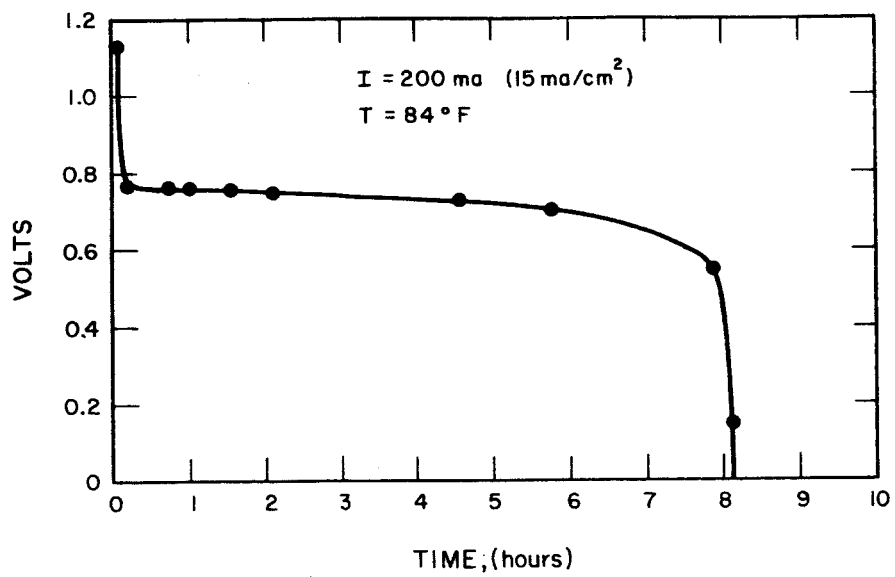


FIG. 14 DISCHARGE OF CELL B AT ROOM TEMPERATURE

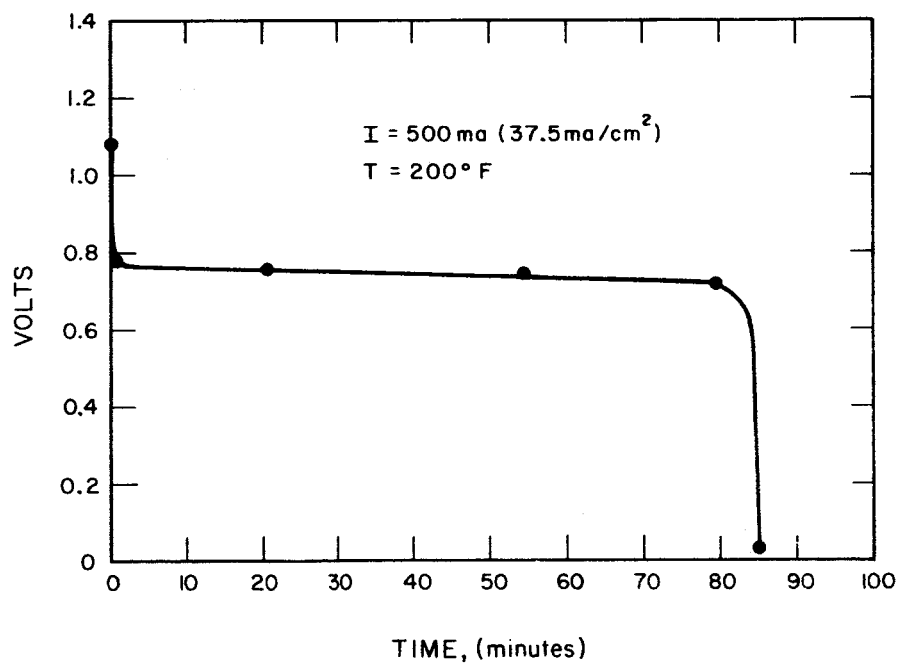


FIG. 15 DISCHARGE OF CELL B AT ELEVATED TEMPERATURE

period of 8 hours. The initial cell pressures for both hydrogen and oxygen were approximately 58 psig. The final pressures, after 8 hours of discharge, were 7 psig.

In Fig. 15 is shown the discharge voltage versus time at 200°F. At this higher temperature the cell can deliver a much higher current density at a given voltage. Therefore, the discharge current was set at 500 ma (37.5 ma/cm^2). As shown the cell voltage remained relatively constant near 0.7 volts for 85 minutes of discharge.

7.15 Capacity of Cell B

The ultimate capacity of cell B has not yet been determined. From the discharge data presented in Sec. 7.14 two values can be calculated: 8 hrs x 0.2 amp or 1.6 amp-hrs and 1.4 hrs x 0.5 or 0.7 amp-hrs. However, these values are not fixed but depend rather on the input to the cell. In a subsequent test in which the cell was charged for a longer period of time, until the gas pressures reached 90 psig, the cell on discharge to a pressure of 10 psig delivered an output of 2.55 amp-hrs (0.2 amps for 12 hrs 45 min).

The limit of the capacity is expected to be the flooding point of the asbestos bed. At this point the water of formation from the electrochemical reaction becomes too large for the bed to contain and the electrodes become flooded. This point will be determined in the near future. The results will be expressed in terms of the capacity per unit area of electrode. The electrode area of the present cell is 13.3 cm^2 or 2.06 in^2 . On the basis of the last value of capacity reported above, the "specific" capacity (amp-hrs/in^2) is found to be $2.55 \text{ amp-hrs}/2.06 \text{ in}^2$ or $1.29 \text{ amp-hrs/in}^2$. This value may be found to be higher when the cell is given a larger charge input. To date the cell has only been charged to pressures of 90 psig, but future plans call for charging to pressures up to 500 psig.

Other factors most likely to affect capacity are the thickness and initial moisture content of the asbestos bed. If the bed thickness were increased or its initial moisture content decreased, the cell capacity could most likely be increased.

Even if the future test results show that the capacity cannot be increased beyond 1.2 amp-hrs/in², it is expected that this limitation will not impose severe limitations on the scale-up of the cell. In fact such a capacity when used in design estimates yields very favorable cell characteristics in terms of amp-hrs or watt-hrs per pound of cell.

7.16 Pressure Variations in Cell B

The pressure versus time relationship for both hydrogen and oxygen has been found to be linear at constant current for both charge and discharge. The slope of the curves corresponds to that which can be calculated on the basis of the known gas volumes, the perfect gas law, and the electrochemical equivalent of the gases. For example, with the known hydrogen volume of 240 cc the hydrogen pressure is calculated to rise 0.662 psi/min at a current of 1.4 amps. Experimentally at 1.4 amps the pressure was found to rise at a rate of 0.659 psi/min in charging from atmospheric to 43.5 psig in exactly 66 minutes. The oxygen pressure was also found to increase at the same rate.

This data tends to verify that the electrochemical reactions are limited to those of the hydrogen-oxygen reactions.

7.17 Oxygen Electrode Evaluation

Since cell B was shown to exhibit appreciable activation polarization and this polarization was attributed to the oxygen electrode, a search was begun to obtain a better oxygen electrode. This search was initiated during the latter portion of the contract period and was carried on simultaneously with the investigation of cell B. Altogether ten different types of oxygen electrodes were evaluated. Of the ten only one, porous carbon impregnated with silver, was found to yield less polarization than the platinized nickel electrode which had been used in all the previous investigations of cell B.

The results of these tests are given below in Table II. The first column gives the type of oxygen electrode, the second gives the open circuit voltage, and the third the operating voltage at a current

density of 5 ma/cm². The porous carbon electrodes (denoted as "P.C.") were 1-5/8 inch diameter and .0625 inch thick. The average pore diameter was .0027 inch and the porosity 40 percent. The porous nickel electrodes (denoted as "P.N.") were 1-5/8 inch diameter and .025 inch thick. The values for pore diameter and porosity have not yet been obtained. The platinum black was applied to the porous nickel electrode by immersion plating in a 3 percent chloroplatinic acid solution. The porous carbon electrodes were impregnated with their respective metal oxide catalysts by immersion in a concentrated solution of the metal nitrate followed by firing in air at 200°C for 6 hours.

TABLE II OXYGEN ELECTRODE EVALUATION

<u>Oxygen Electrode Type</u>	<u>Open Circuit Voltage</u>	<u>Voltage at 5 ma/cm²</u>
1. P.C. (no catalyst)	0.82	0.47
2. P.C. + silver	1.15	0.83
3. P.C. + copper	0.90	0.28
4. P.C. + cobalt	0.92	0.42
5. P.C. + chromium	0.90	0.20
6. P.C. + nickel	0.35	0.00
7. P.C. + iron	0.89	0.00
8. P.N. + platinum black at 5 mg/in ²	0.86	0.48
9. P.N. + platinum black at 20 mg/in ²	0.92	0.65
10. P.N. + platinum black at 40 mg/in ²	0.92	0.65

The criterion for the selection of the best electrode is the operating voltage at a given load. As indicated in Table II the porous carbon electrode impregnated with silver gave a significantly higher operating voltage than any of the others and may therefore be classified as the best of the ten. The next best electrode was found to be the porous nickel coated with platinum black. The amount of platinum black at levels between 20 and 40 mg/in² does not appear to affect the voltage.

However, at a density of 5 mg of platinum black per square inch the open circuit and operating voltage dropped significantly.

The open circuit voltages cannot be used in predicting the performance of the cell under load. The values, however, have been reported for the sake of completeness.

8. IMPORTANT ACCOMPLISHMENTS

The analysis of the cause for the rapid loss of charge of cell A suggested several modifications for overcoming this limitation. Consideration of all the factors led to the design of cell B. Upon assembly and evaluation of this cell model the result was verified that this particular cell design displayed much better charge retention. The modifications which led to the design of cell B constituted one of the major accomplishments during this program.

Since the first model of cell B was constructed of plastic and glass, the operating pressures were necessarily restricted to rather low values. Subsequently however a stainless steel model was assembled for operation at higher pressures. Upon evaluation of this model at high pressure the result was established that its capacity was much greater than that of cell A. The large improvement in cell capacity constituted a second important accomplishment.

Also worthy of note is the experimental evidence which has been obtained to support the belief that the electrochemical reactions within both cells A and B are limited to those of the hydrogen-oxygen reactions. These results therefore permit the classification of the EOS cell as a "regenerative hydrogen-oxygen cell" and thereby define the theoretical characteristics of this cell, i.e., open circuit voltage and capacity per unit weight.

The studies of cell polarization have yielded significant results. The most important conclusion was that activation polarization constituted a large portion of the total cell polarization. Since the activation polarization is primarily a function of the properties of the electrodes, the area for improvement is clearly defined. The brief study of oxygen electrodes during the latter portion of the program has yielded some encouraging results but a considerable amount of investigation remains to be done before definite conclusions can be made.

9. IMPORTANT PROBLEM AREAS

A review of the characteristics of cell B indicates that there are two important problem areas where future efforts should be concentrated. The first area is that of polarization or voltage efficiency. A reasonable efficiency for which to strive would be 70 percent or 80 percent. The approach to this problem undoubtedly lies in the development of a better oxygen electrode. Therefore the electrode studies should be continued. Consideration should also be given to new oxygen electrodes being developed by other laboratories.

The second problem area is that of charge retention. Although the results obtained to date are much better than at the beginning of the program, additional improvements in charge retention would permit more general application of the cell. A thorough study of the effects of temperature, pressure, and bed thickness on charge retention would indicate the extent of the improvements that can be made.

10. CONCLUSIONS

- a. The modifications incorporated in the design of cell B* greatly increase the charge retention over that of cell A.
- b. The same modifications resulted in a much higher capacity for cell B as compared with cell A.*
- c. Appreciable activation polarization is present in both cells A and B.
- d. The ohmic polarization is relatively small for both cells A and B at elevated temperatures. The ohmic polarization of cell B is appreciable near room temperature.
- e. The observed characteristics of both cells A and B give support to the belief that the electrochemical reactions within the cell are limited to those of the hydrogen and oxygen half-cell reactions.

*Refer to Section 6 for description of cells A and B.

* Refer to Section 6 for description of cells A and B.

11. FUTURE PROGRAM

The next program for the continued development of this fuel cell should be carried out in two areas. The first area should consist of a continued evaluation of all the factors affecting charge retention. The important factors and suggested range of conditions are tabulated below:

Temperature: 70°F to 300°F
Pressures: 0 to 500 psig
Bed Thickness: 1/32 inch to 1/4 inch
Stand Times: 0 to 72 hours

The second area should consist of an evaluation of alternative oxygen electrodes. Some suggested electrodes are porous carbon or porous nickel impregnated with suitable catalysts such as platinum black or palladium black.

Other likely catalysts are the spinels as described by Kordesch (Ref. 9). The level of catalyst addition as well as the pore size and pore size distribution of the porous carbon or porous nickel should also be examined.

In addition to these investigations, tests should be made by operation of multiple cells in electrical combinations.

When the results of the above studies have advanced to the point where the performance characteristics of the cell are deemed suitable by the contract monitor, a flight-weight model should be designed, fabricated and tested to specifications provided by the contract monitor.

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